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Dependence of configurational properties on the degree of polymerization

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# Monte Carlo studies of the excluded volume problem for polymer chains in the continuum II. Dependence of configurational properties on the degree of polymerization

N C Smith and R J Fleming

Department of Physics, Monash University, Clayton, Victoria 3168, Australia

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**Abstract.** Using the inversely restricted sampling techniques described in the previous paper, three-dimensional continuum model chains up to 1000 links in length have been generated, with both freely varying and fixed bond angles. An analysis of their configurational properties leads to the following conclusions.

(i) The geometric expansion of intermediate length ( $\leq 100$  links) chains due to excluded volume effects increases monotonically with the volume of the spheres representing the individual monomer units of the chain.

(ii) The expansion factor  $\alpha^2(N) = \langle R_N^2 \rangle / \langle R_N^2 \rangle_0$ , where  $\langle R_N^2 \rangle_0$  is the mean square end-to-end length of  $N$ -link chains at zero excluded volume, does not consistently follow (for  $N \leq 100$  and  $v \leq 1.0$ ) any of the published two-parameter curves, eg those of Flory and Fisk.  $v$  is the excluded volume ratio.

(iii) The ratio  $\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$ , where  $\langle S_{100}^2 \rangle$  is the mean square radius of gyration of 100-link chains, decreases slowly from 0.167 at zero excluded volume to about 0.157 for  $v \geq 0.6$ , these values being very close to those published for on-lattice chains.

(iv) The distribution function  $W(R)$  of the probability that the end-to-end length of a chain will be  $R$  can be expressed as  $W(R) dR = KR^2 \exp[-(R/\sigma)^t] dR$  where  $K$  and  $\sigma$  are constants, the latter being directly proportional to the mean square end-to-end length of the chain, and  $t$  is a parameter which increases monotonically with increasing excluded volume from a value of 2.0 at zero excluded volume.

## 1. Introduction

In the previous paper (Smith and Fleming 1975, to be referred to as I) we described the use of inversely restricted sampling techniques in computer generation of model polymer chains subject to excluded volume restraints, but not, as in most other Monte Carlo studies, constrained to lie on a regular crystalline lattice. The purpose of this paper is to present the results of our calculations of the dependence of the configurational properties of such chains on the degree of polymerization, ie on the number of links  $N$  in the chains. In § 2 we discuss the dependence of the mean square end-to-end length  $\langle R_N^2 \rangle$  and the mean square radius of gyration  $\langle S_N^2 \rangle$  of  $N$ -link chains on  $N$ , and the behaviour of the ratio  $\langle S_N^2 \rangle / \langle R_N^2 \rangle$ , up to  $N = 100$ . Relative weighting problems inherent in the inversely restricted sampling technique prevented the acquisition of reliable data on  $\langle R_N^2 \rangle$  and  $\langle S_N^2 \rangle$  for  $N > 100$ . Section 3 is devoted mainly to a comparison of the long- and short-range effects of excluded volume in longer chains, and in § 4 we deduce

a possible form for the distribution function of the chain end-to-end length. General discussion of the results follows in § 5, and the overall conclusions drawn from this study are stated in § 6.

### 2. Simple geometric properties of 100-link chains

$\langle R_N^2 \rangle$  was computed from the equation

$$\langle R_N^2 \rangle = \frac{\sum_{i=1}^m (R_N^2/p_i)}{\sum_{i=1}^m p_i^{-1}}$$

where  $p_i$  is the multiplicity (see I) of the  $i$ th chain of a sample containing  $m$  chains. A similar equation holds for  $\langle S_N^2 \rangle$ .

The  $\langle R_N^2 \rangle$  results for 100-link chains are presented in figures 1 and 2 for three values of the excluded volume ratio  $v$  defined in I. The dots represent the computer-generated or 'experimental' values of  $\langle R_N^2 \rangle$ , while the continuous lines represent least-squares fits of these values to the relationship

$$\langle R_N^2 \rangle = aN^\gamma. \tag{1}$$

These fits were obtained by two distinct methods, firstly by the obvious linearization

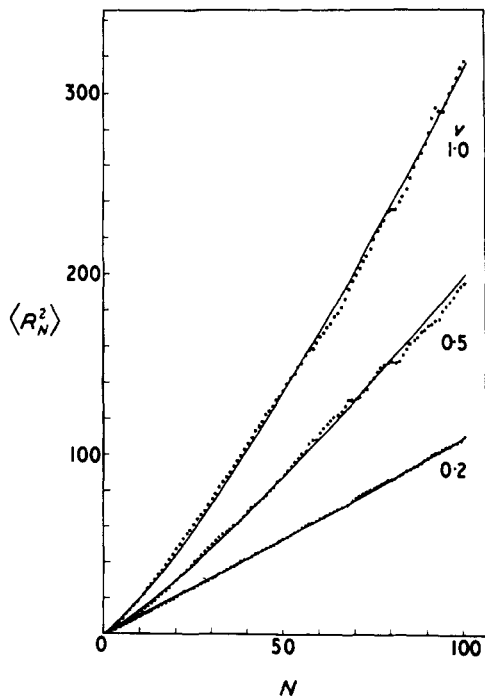


Figure 1. Dots: computer-generated  $\langle R_N^2 \rangle$  data for freely varying bond angles. Full curves: least-squares fits of  $\langle R_N^2 \rangle = aN^\gamma$  to the computer-generated data. See table 1 for  $a$  and  $\gamma$  values.

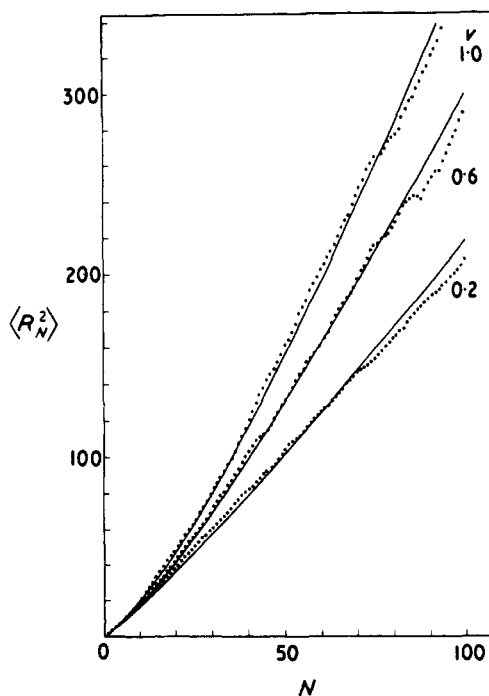


Figure 2. Dots: computer-generated  $\langle R_N^2 \rangle$  data for fixed bond angles. Full curves: least-squares fits of  $\langle R_N^2 \rangle = aN^\gamma$  to the computer-generated data. See table 1 for  $a$  and  $\gamma$  values.

of equation (1) yielding

$$\ln \langle R_N^2 \rangle = \ln a + \gamma \ln N,$$

and, secondly, using a computer program (Burroughs 1964) which minimizes the relative error

$$(\langle R_N^2 \rangle_{\text{exp}} - \langle R_N^2 \rangle_{\text{calc}})^2 / \langle R_N^2 \rangle_{\text{exp}}$$

through the first and second partial derivatives of the function  $aN^\gamma$ . The relative error was minimized, rather than the error, in order to avoid giving undue weight to the data for large  $N$ . The  $\gamma$  values derived from these two methods agreed with each other to the third decimal place. The excluded volume ratio  $v$  was varied in steps of 0.1 from 0.2 to 1.0 inclusive, 2000 chains being generated at  $v = 0.2, 0.4$ , etc, and 1000 chains at  $v = 0.3, 0.5$ , etc. All the fixed bond angle results were obtained from 1000-chain samples, for  $v$ -increments of 0.2, since  $\langle R_N^2 \rangle$  varies more slowly with  $v$  in this case. The values of  $a$  and  $\gamma$  are presented in table 1, the fourth column being the average percentage difference between the computer-generated  $\langle R_N^2 \rangle$  and the values calculated from equation (1) using the quoted  $a$  and  $\gamma$  values. These percentage differences are presented in order to give an alternative indication of the accuracy of the fit of equation (1) to the data. The fractional error in the mean value of the computer-generated  $\langle R_N^2 \rangle$ , defined as the ratio (standard error in  $\langle R_N^2 \rangle$ )/ $\langle R_N^2 \rangle$ , remained approximately constant for  $N > 20$  in both bond angle models. This result suggests that a given number of chain samples yields the same accuracy for all chain lengths, there being no discernible effect of the decrease in statistical weight with increasing length due to use of the inversely restricted sampling technique.

It will be seen that: (i) the  $\gamma$  values for fixed bond angle chains are consistently larger, at the same  $v$  values, than those for freely varying bond angle chains; (ii) there

**Table 1.** Values of  $a$  and  $\gamma$  in  $\langle R_N^2 \rangle = aN^\gamma$ , for various values of  $v$ .

Excluded volume ratio $v$	$\gamma$	$a$	$E(\%)$
Freely varying bond angles			
0.2	1.026	0.973	1.77
0.3	1.089	0.898	2.48
0.4	1.092	0.967	1.66
0.5	1.165	0.928	2.17
0.6	1.186	0.936	1.57
0.7	1.173	1.105	2.07
0.8	1.193	1.139	1.56
0.9	1.243	1.076	2.07
1.0	1.208	1.210	1.55
Fixed bond angles			
0.2	1.100	1.384	2.40
0.4	1.141	1.326	2.22
0.6	1.193	1.234	2.14
0.8	1.230	1.208	2.01
1.0	1.255	1.160	1.98

is generally a steady increase in  $\gamma$  with increasing  $v$  for both models. (The data for  $v = 0.9$  in the freely varying bond angle case are thought to be non-representative.) However, the relatively small number of samples limits the accuracy of the results. More importantly, the quoted  $\gamma$  values may simply be effective exponents at low  $N$ , the true asymptotic behaviour being attained only at much higher  $N$ . This point is taken up in § 3.

The variation of  $\langle S_N^2 \rangle$  with  $N$  is shown in figures 3 and 4. Writing

$$\langle S_N^2 \rangle = a'N^{\gamma'}$$

the corresponding least-squares data appear in table 2. Figures 3 and 4 are noticeably smoother than figures 1 and 2, as might be expected, since the values of  $S_N^2$  for a particular chain are derived from the configuration of the whole chain, rather than from its end-points alone. The observations (i) and (ii) for  $\langle R_N^2 \rangle$  appearing in the preceding paragraph are clearly valid for  $\langle S_N^2 \rangle$ . The  $\gamma'$  values are consistently smaller than the corresponding  $\gamma$  values, contrasting with lattice-constrained chains for which  $\gamma' = \gamma$ . However, it may be that  $\gamma'$ , like  $\gamma$ , has not reached its asymptotic values at  $N = 100$ . Even in a chain with no excluded volume constraints  $\langle S_N^2 \rangle$  tends to its asymptotic behaviour much more slowly than  $\langle R_N^2 \rangle$ ; perhaps excluded volume effects further slow this approach. The result  $\gamma' = 0.966$  at  $v = 0.2$  in the freely varying bond angle case certainly supports this suggestion, since the asymptotic value of  $\gamma'$  is unity for zero excluded volume.

The variation of the ratio  $\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$  with  $v$  is shown in table 3. Clearly, since  $\gamma'$  is always less than  $\gamma$ , as stated above for 100-link chains, this ratio must decrease steadily with increasing  $N$ . However, beyond  $v = 0.6$  it does not appear to vary in any consistent fashion with increasing  $v$ , the average value being 0.157 for both geometries.

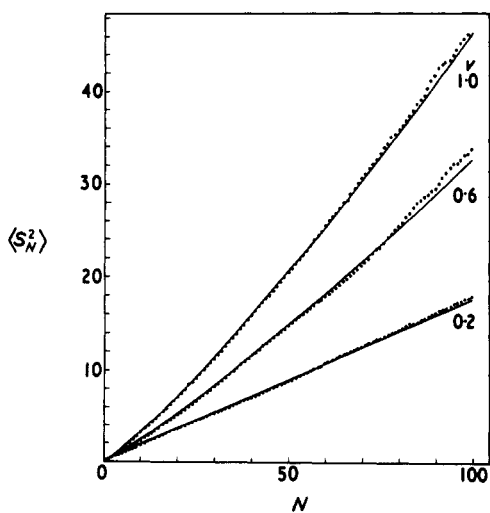


Figure 3. Dots: computer-generated  $\langle S_N^2 \rangle$  data for freely varying bond angles. Full curves: least-squares fits of  $\langle S_N^2 \rangle = a'N^{\gamma'}$  to the computer-generated data. See table 2 for  $a'$  and  $\gamma'$  values.

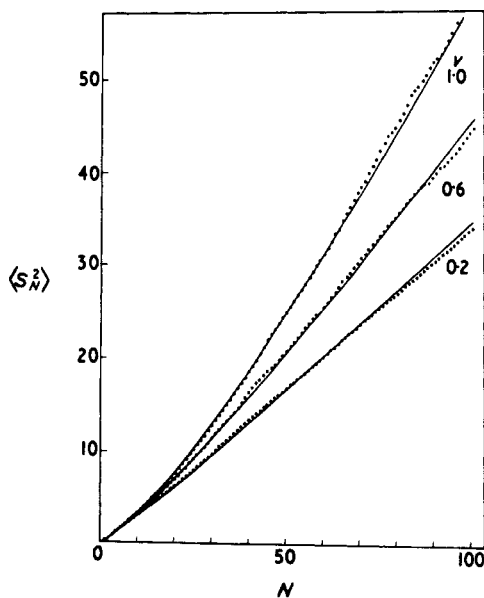


Figure 4. Dots: computer-generated  $\langle S_N^2 \rangle$  data for fixed bond angles. Full curves: least-squares fits of  $\langle S_N^2 \rangle = a'N^{\gamma'}$  to the computer-generated data. See table 2 for  $a'$  and  $\gamma'$  values.

**Table 2.** Values of  $a'$  and  $\gamma'$  in  $\langle S_N^2 \rangle = a'N^{\gamma'}$ , for various values of  $v$ .

Excluded volume ratio $v$	$\gamma'$	$a'$	$E(\%)$
Freely varying bond angles			
0.2	0.966	0.207	1.53
0.4	1.025	0.202	1.42
0.6	1.118	0.188	1.33
0.8	1.122	0.217	1.29
1.0	1.159	0.223	1.30
Fixed bond angles			
0.2	1.067	0.258	1.39
0.4	1.114	0.238	1.36
0.6	1.156	0.226	1.31
0.8	1.202	0.213	1.25
1.0	1.242	0.195	1.24

**Table 3.** Variation of the ratio  $\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$  with  $v$ .

Excluded volume ratio $v$	$\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$ for freely varying bond angles	$\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$ for fixed bond angles
0.0 (unrestricted random walk)	0.168	0.166
0.2	0.162	0.160
0.4	0.162	0.158
0.6	0.155	0.158
0.8	0.160	0.155
1.0	0.157	0.158

The same or very similar figures have been reported by several authors for lattice-constrained chains, eg Wall and Erpenbeck (1959) obtained 0.157 for 600-link chains on a tetrahedral lattice, Gallacher and Windwer (1966) obtained 0.157 for 200-link branched chains after an induction length of about 75 links, and Windwer (1965) obtained 0.158 for 96-link chains on a variable lattice. The latter author concluded that the ratio was independent of model, and the present results would appear to support him.

In order to check the reliability of the inversely restricted sampling data, 120-link chains were generated, with both freely varying and fixed bond angles, at  $v = 0.2$ , any chain being discarded immediately it violated the excluded volume conditions. The results should be free of systematic statistical bias, their accuracy being limited only by the sample size. (More than 10 000 chains of 120 links were generated for each geometry.) The  $\langle R_N^2 \rangle$  and  $\langle S_N^2 \rangle$  values agreed with the inversely restricted sampling data to well within the expected error set by the rather small sample size in the latter case. We may therefore have confidence in the reliability of the inversely restricted sampling data at higher values of  $v$ .

As an alternative method of analysis of the expansion of the chains due to excluded volume effects, the data were compared with the predictions of the perturbation theory formulation of the excluded volume problem, based on the use of pseudopotentials

(Zimm 1946). This formulation is applicable to both lattice and continuum models and yields

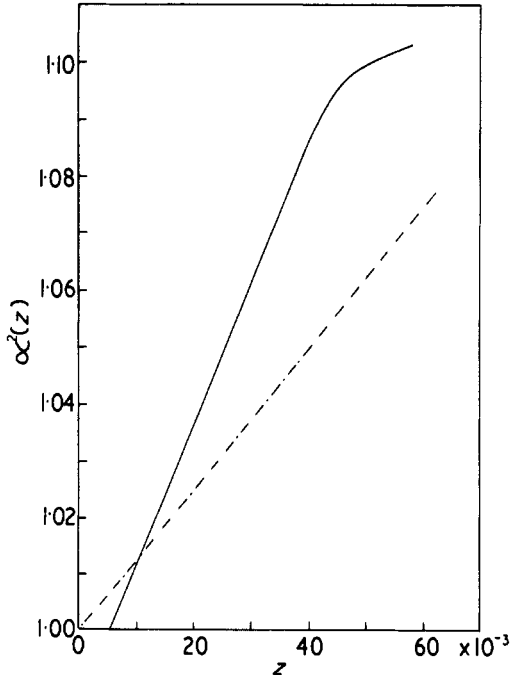
$$\alpha^2(z) = \frac{\langle R_N^2 \rangle}{\langle R_N^2 \rangle_0} = 1 + A_1 z + A_2 z^2 + A_3 z^3 + \dots \tag{2}$$

where  $\langle R_N^2 \rangle_0$  is the mean square end-to-end length of an  $N$ -link chain with zero excluded volume, and

$$z = \left( \frac{3}{2\pi b^2} \right)^{3/2} \beta N^{1/2},$$

$b$  being the link length and  $\beta$  the binary cluster integral.  $\beta$  represents the effective excluded volume. The above expansion is valid only for  $N \rightarrow \infty$ ,  $\beta \rightarrow 0$ ,  $\beta N^{1/2}$  finite, and is usually called the two-parameter approximation. According to Yamakawa (1971) it can be used up to  $z = 0.15$ ; the same author quotes values for  $A_1$ ,  $A_2$  and  $A_3$ , the only coefficients known exactly. Many authors (Flory 1949, Flory and Fisk 1966, Yamakawa and Tanaka 1967, Alexandrowicz 1967, 1968, Kurata 1968) have provided closed-form alternatives to equation (2) which are supposed to be valid over the entire range of  $z$ , although still subject to the condition  $N \gg 1$ . Recently, Domb *et al* (1973) have derived numerical estimates of  $\alpha^2(z)$  which are expected to remain valid for all  $N$ . There is very little difference between these various approximations at small  $z$ , but the discrepancies become very marked as  $z$  increases (Alexandrowicz and Accad 1973).

In figure 5 we compare the Monte Carlo values (the set in which a chain was discarded immediately it violated the excluded volume conditions) of  $\alpha^2(z)$  for chains



**Figure 5.** Expansion factor  $\alpha^2(z)$  for chains with freely varying bond angles,  $v = 0.2$ . Full curve: Monte Carlo data; chain curve: Alexandrowicz (1968) two-parameter approximation.

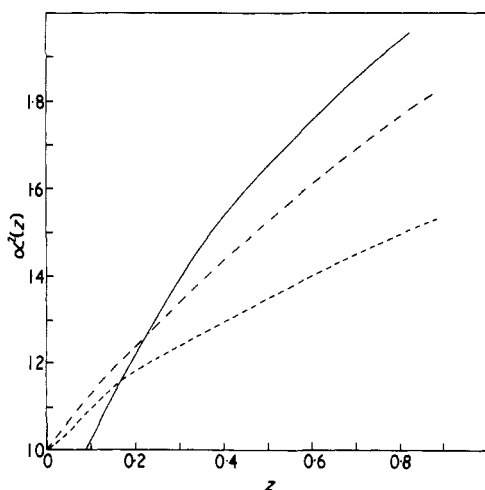
with freely varying bond angles at  $v = 0.2$  (low  $z$ ) with those given by a representative two-parameter expression (Alexandrowicz 1968)

$$\frac{\alpha^5}{5} + \frac{\alpha^3}{3} - \frac{8}{15} = \frac{4z}{3}.$$

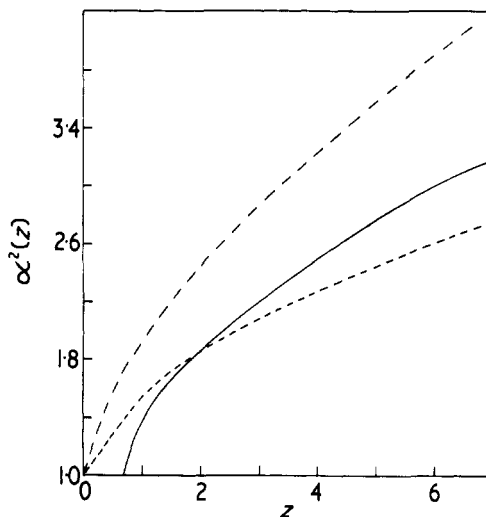
The excluded volume parameter  $\beta$  was taken as four times the volume of the sphere representing a repeat unit of the chain (Fowler and Guggenheim 1939);  $\langle R_N^2 \rangle_0$  was equated to  $N$ . It will be seen that, except at very low  $z$ , the Monte Carlo  $\alpha^2(z)$  values are consistently larger than those predicted by the two-parameter approximation. Since the Monte Carlo values were obtained by averaging over more than 10 000 chains, it is very unlikely that the difference can be completely accounted for on statistical grounds. Of course the two-parameter theory holds formally only for large  $N$ ; however the  $\alpha^2(z)$  values of Domb *et al* (1973), which as stated earlier are expected to be valid for all  $N$ , differ only very slightly from those of Alexandrowicz at small  $N$ . Since the calculations of Domb, Barrett and Lax were performed specifically for a Gaussian distribution of bond lengths, a large number of chains with such a distribution were generated, using the Monte Carlo technique, in order that a meaningful comparison could be made. The resulting  $\alpha^2(z)$  values followed those for a constant bond length very closely.

Similar comparisons for  $v = 0.5$  and  $1.0$  are shown in figures 6 and 7 respectively, using the inversely restricted sampling Monte Carlo data. Of the various two-parameter approximations for  $\alpha^2(z)$ , that of Alexandrowicz (1968) gives the largest values, and that of Flory and Fisk (1966) the smallest. It will be seen that the Monte Carlo data do not consistently follow either; the same is true for the other approximations.

It would thus appear very unlikely that, for  $N \leq 100$ , any of the two-parameter  $\alpha^2(z)$  approximations will accurately represent the expansion of chains with freely varying bond angles constructed in the continuum, over the range of  $v$  up to  $1.0$ . It is



**Figure 6.** Expansion factor  $\alpha^2(z)$  for chains with freely varying bond angles,  $v = 0.5$ . Full curve: Monte Carlo data; chain curve: Alexandrowicz (1968) two-parameter approximation; broken curve: Flory and Fisk (1966) two-parameter approximation.



**Figure 7.** Expansion factor  $\alpha^2(z)$  for chains with freely varying bond angles,  $v = 1.0$ . Full curve: Monte Carlo data; chain curve: Alexandrowicz (1968) two-parameter approximation; broken curve: Flory and Fisk (1966) two-parameter approximation.



particularly noteworthy that the virial expansion for  $\alpha^2(z)$  at low  $z$  (equation (2)) also fails. It may be that the total excluded volume is not simply four times the volume of the sphere representing the repeat unit of the chain (the intrinsic excluded volume), but contains an additional as yet unknown component due to the extrinsic excluded volume (see § 3). The situation in the fixed bond angle case is even more complex, and therefore no analysis of  $\alpha^2(z)$  was attempted for that geometry.

### 3. Short- and long-range effects of excluded volume in longer chains: inversely restricted sampling technique

Unfortunately, attempts to obtain data on  $\langle R_N^2 \rangle$  and  $\langle S_N^2 \rangle$  for  $N > 100$ , using the inversely restricted sampling technique, proved unsuccessful. Two thousand 500-link chains with freely varying bond angles and  $v = 0.5$ , and one thousand chains with  $v = 1.0$ , were constructed. The variation of  $\langle R_N^2 \rangle$  with  $N$  for  $v = 0.5$  becomes erratic beyond  $N = 160$  approximately. This erratic behaviour occurs at lower  $N$  for greater  $v$ , eg  $N = 110$  at  $v = 1.0$ , and is due to a deficiency inherent in the inversely restricted sampling technique, as pointed out by Rosenbluth and Rosenbluth (1955). The range in magnitude of the statistical weights of the chains increases rapidly with  $N$ , since the weight of each  $N$ -link configuration is computed as a  $\pi$ -product of  $N$  fractions. Thus at large  $N$  the cumulative effect of small differences in individual link weights can be very large. Figure 8 is a histogram of the weights found in five hundred 500-link chains with freely varying bond angles at  $v = 0.5$ , and shows that a large variation in weights does occur in practice. The long tail of low-weight chains will not significantly affect the average values of  $\langle R_N^2 \rangle$  and  $\langle S_N^2 \rangle$ ; these parameters are therefore dominated by the relatively few chains with high weights found at the other end of the distribution, and hence the calculated average values could be considerably in error. However, analysis of the two thousand chain sample up to  $N = 500$ , with normal weighting, yielded  $\gamma = 1.15$ ,  $a = 1.01$ , in reasonable agreement with the corresponding figures shown in table 1, despite the small effective number of samples.

Clearly, very large numbers of chains would have to be generated, especially at high values of  $v$ , in order to obtain sufficient high-weight chains so that statistically reliable  $\langle R_N^2 \rangle$  and  $\langle S_N^2 \rangle$  data could be extracted, say up to  $N = 200$ . The enormous amount of computing time required to accomplish this was not available, and therefore an attempt to obtain this information, using the sample enrichment technique of Wall and Erpenbeck (1959), was made.

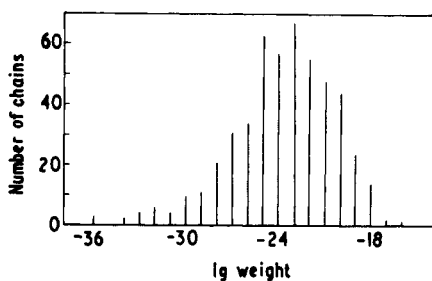


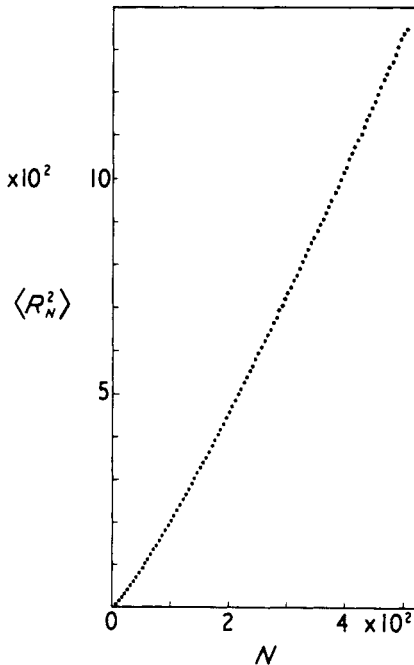
Figure 8. Histogram of the number of weights of each order found in a sample of five hundred 500-link chains with freely varying bond angles, at  $v = 0.5$ .

### 3.1. Sample Enrichment Technique

It has been found (Wall *et al* 1954, 1955, 1957) that, for on-lattice model chains, if  $C_t$  and  $C_{t+s}$  are the number of  $t$ -link and  $(t+s)$ -link chains respectively, then

$$C_{t+s} = C_t \exp(-\lambda s) \quad (3)$$

where  $\lambda$  is the attrition constant characteristic of the particular lattice. Thus by using a short  $s$ -link chain  $p$  times as a stem to which are added a further  $s$  links, where  $p \simeq \exp(\lambda s)$ ,  $p$  and  $s$  being of necessity integers, one can largely overcome loss of samples through violation of the excluded volume conditions. Ideally  $p$  should be slightly less than  $\exp(\lambda s)$  in order to avoid population 'explosion'. Equation (3) was found to hold fairly accurately for freely varying bond angle chains, and  $\lambda$  was evaluated as 0.149 at  $v = 0.5$  by generating large numbers of short chains (up to 20 links) and discarding any chain immediately it violated the excluded volume conditions. Thus  $s = 14$  and  $p = 8$ . Two thousand nine hundred 504-link chains were then generated using the sample enrichment technique with these parameters, each chain having thirty-six 14-link sections. The resulting variation of  $\langle R_N^2 \rangle$  with  $N$  is shown in figure 9, the corresponding values of  $a$  and  $\gamma$  being  $0.95 \pm 0.18$  and  $1.165 \pm 0.003$  respectively. These values agree well with those shown in table 1, suggesting that, as far as the exponent  $\gamma$  is concerned, chains with freely varying bond angles and  $v = 0.5$  have attained asymptotic behaviour at  $N = 100$ . However, this result must be treated with some reservation, since slight population occurred, indicating an overestimate of  $\lambda$ . This overestimate probably arose from the use of too short ( $N \leq 20$ ) or too few chains in the estimation process.



**Figure 9.**  $\langle R_N^2 \rangle$  against  $N$  for 504-link chains with freely varying bond angles and  $v = 0.5$ , generated using the sample enrichment technique of Wall and Erpenbeck.

Hence there may be too much resemblance between 'families' of chains, because of their common stems, and the results may therefore be unduly biased (Domb 1963).

The sample enrichment technique was not pursued further since, even at  $v = 0.5$ , sixteen hours of computer time were required to generate the two thousand nine hundred chains to which figure 9 relates. This time would increase, of course, for higher  $v$ . The total time requirement is even greater, since, for each value of  $v$ , large numbers of short chains must be generated in order to estimate the attrition constant  $\lambda$  sufficiently accurately.

### 3.2. Attrition constants and percentage excluded locus

Fortunately, in the course of analysis of the statistical weights of chains generated using the inversely restricted sampling technique, a trend was observed which suggested an alternative though less direct approach to the problem. This approach appears to avoid the necessity of generating very large numbers of high-weight chains.

Figure 10 shows the variation with  $N$  of the logarithm of the maximum, minimum, and mean weights of the sample of five hundred 500-link chains to which figure 8 refers.

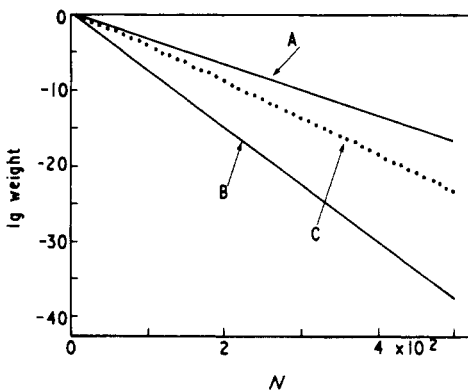


Figure 10. Variation with  $N$  of the logarithm of the maximum (A), minimum (B), and mean (C) weights of the same chain sample as figure 8.

Defining  $\lg(\text{weight})$  as the order of the weight, then it will be seen that, apart from slight curvature at very low  $N$ , the mean of the order of the weights  $M_N$  (shown as full circles in figure 11) is approximately proportional to  $N$ , that is

$$M_N = \sum_{k=1}^C \frac{1}{C} \lg W_{N_k} \approx gN \quad (4)$$

where  $C$  is the number of chains in the sample,  $g$  is a constant and  $W_{N_k}$  is the weight of the  $k$ th  $N$ -link chain in the sample:

$$W_{N_k} = \prod_{i=1}^N S_{ik}$$

$S_{ik}$  is the proportion of the locus of the centre of the  $(i+1)$ th monomer in the  $k$ th chain

which is not excluded. Then

$$M_N = \sum_{k=1}^C \frac{1}{C} \lg W_{N_k} = \lg(W_{N_1} W_{N_2} \dots W_{N_C})^{1/C}.$$

Since  $M_N$  is proportional to  $N$  at large  $N$ ,

$$\begin{aligned} \frac{\lg(W_{N_1} W_{N_2} \dots W_{N_C})^{1/C}}{N} &= \frac{\lg([S_{11} S_{21} \dots S_{N1}][S_{12} S_{22} \dots S_{N2}] \dots [S_{1C} S_{2C} \dots S_{NC}])^{1/C}}{N} \\ &\simeq \text{constant,} \quad \text{at large } N. \end{aligned}$$

Hence

$$\begin{aligned} \frac{\lg([S_{11} S_{21} \dots S_{m1}][S_{12} S_{22} \dots S_{m2}] \dots [S_{1C} S_{2C} \dots S_{mC}])^{1/C}}{m} \\ \simeq \frac{\lg([S_{11} S_{21} \dots S_{m+1,1}][S_{12} S_{22} \dots S_{m+1,2}] \dots [S_{1C} S_{2C} \dots S_{m+1,C}])^{1/C}}{m+1}. \end{aligned}$$

Re-grouping the products

$$\begin{aligned} \frac{\lg([S_{11} S_{12} \dots S_{10}][S_{21} S_{22} \dots S_{2C}] \dots [S_{m1} S_{m2} \dots S_{mC}])^{1/C}}{m} \\ \simeq \frac{\lg([S_{11} S_{12} \dots S_{1C}][S_{21} S_{22} \dots S_{2C}] \dots [S_{m+1,1} S_{m+1,2} \dots S_{m+1,C}])^{1/C}}{m+1}. \end{aligned}$$

Hence

$$\frac{\sum_{i=1}^m \lg[(S_{i1} S_{i2} \dots S_{iC})^{1/C}]}{m} \simeq \frac{\sum_{i=1}^{m+1} \lg[(S_{i1} S_{i2} \dots S_{iC})^{1/C}]}{m+1}.$$

If this is to be true for all  $m$ , then

$$\lg[(S_{m1} S_{m2} \dots S_{mC})^{1/C}] \simeq \lg[(S_{m+1,1} S_{m+1,2} \dots S_{m+1,C})^{1/C}]$$

or

$$\lg[(S_{N1} S_{N2} \dots S_{NC})^{1/C}] \simeq \text{constant}$$

except at very small values of  $N$ . Now the  $S_{Ni}$  are independent of each other, since they relate to different chains. We may deduce that the  $S_{Ni}$  are approximately constant for all but the smallest values of  $N$ , and may be denoted  $\langle S \rangle$ . Hence

$$M_N \simeq N \lg \langle S \rangle \dots \quad (5)$$

The average proportion of the spherical locus available to the centre of each monomer may thus be found from the gradient of a plot of  $M_N$  against  $N$ . Comparison of equations (4) and (5) gives

$$\langle S \rangle = 10^{-8}.$$

Direct inspection of the average proportion of the locus available to each monomer, in chains with freely varying bond angles at  $v = 0.5$ , verified that  $\langle S \rangle$  was constant throughout the range  $N = 15-500$ . The agreement was remarkable, the average proportion of the locus available varying only by  $\pm 0.015$  from the value 0.851 found for  $\langle S \rangle$  from the slope of the  $M_N$  against  $N$  plot. Corresponding results were obtained for other values of  $v$ .

It is now clear why, when using the sample enrichment technique, equation (3) (originally deduced for on-lattice chains) was found to be valid. The probability  $P_N$  of failure at the  $N$ th link, due to excluded volume restraints, is given by

$$P_N = 1 - \langle S_N \rangle = 1 - \langle S \rangle = P \quad (N > 15).$$

Thus the probability that a chain of more than 15 links will survive the addition of a further  $s$  links is

$$\begin{aligned} (1 - P)^s &= \exp[s \ln(1 - P)] \\ &= \exp[-s(P + \frac{1}{2}P^2 + \frac{1}{3}P^3 + \dots)] \quad \text{since } P < 1. \end{aligned}$$

Hence

$$C_{t+s} = C_t \exp[-s(P + \frac{1}{2}P^2 + \frac{1}{3}P^3 + \dots)],$$

and we can equate the attrition constant  $\lambda$  in equation (1) to the series  $P + \frac{1}{2}P^2 + \frac{1}{3}P^3 + \dots$ . However it has been customary (Wall *et al* 1954, Alexandrowicz 1969) to equate  $\lambda$  and  $P$ , although Hammersley and Morton (1954) showed that equation (3) is exact only in the limit of large  $t$ . Hence  $\lambda$  derived from the ratio  $C_{t+s}/C_t$  would be expected to be approximately  $(1 + P/2)$  times the value obtained from the equation  $\lambda = 1 - \langle S \rangle$ . In fact the two methods yield identical values in the case of freely varying bond angle chains at  $v = 0.5$ , ie  $\lambda = 0.149$  from the former, and  $\lambda = 1 - 0.851 = 0.149$  from the latter. However, as mentioned above, very short ( $N \leq 20$ ) chains were used in the former method, because of limited computing time, and it may well be that  $\lambda$  increases with  $N$  until asymptotic behaviour is attained.

The variation of  $\lambda$  with  $v$ , deduced from the mean weights of 100-link chains, is shown in figure 11. It will be seen that  $\lambda$  increases approximately linearly with  $v$ , both for freely varying and fixed bond angles.

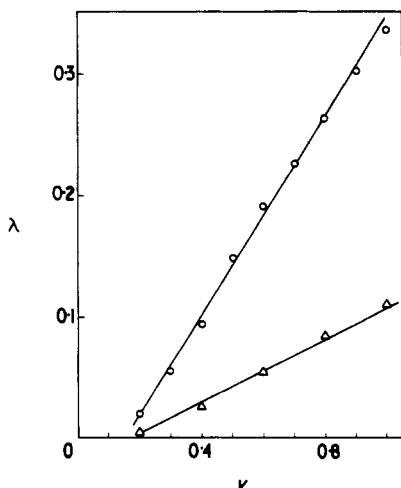


Figure 11. Variation of attrition constant  $\lambda$  with  $v$  for 100-link chains.  $\circ$ , freely varying bond angles;  $\triangle$ , fixed bond angles.

The observation of a constant probability of violation of the excluded volume conditions in continuum-model chains, at sufficiently large  $N$ , is of fundamental importance. The validity of the attrition law (equation (3)), and the deduction therefrom of a constant probability of intersection, has of course long been recognized for lattice-model chains. However, it was not clear that constant probability of self-intersection of a lattice-model chain was not due to the regular lattice structure. It would now appear that this constant probability is a characteristic of the chains themselves.

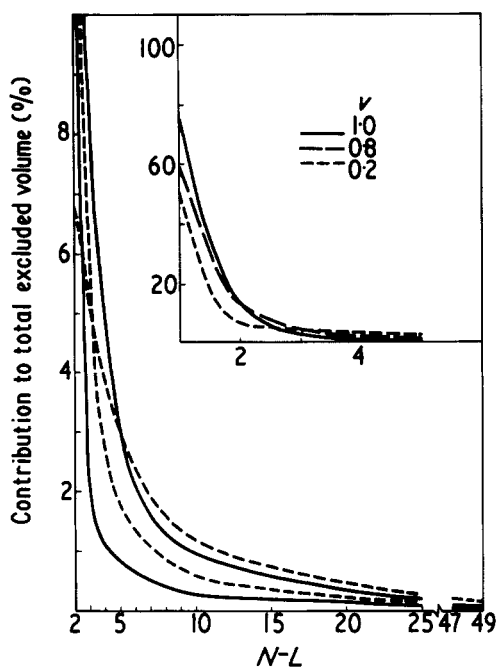
### 3.3. Dual nature of excluded volume

In order to investigate the range over which excluded volume effects are operative, the proportions of the locus of the centre of each monomer, say for example, the  $(N + 1)$ th, excluded by the  $(N - 1)$ th,  $(N - 2)$ th, etc monomers were determined.

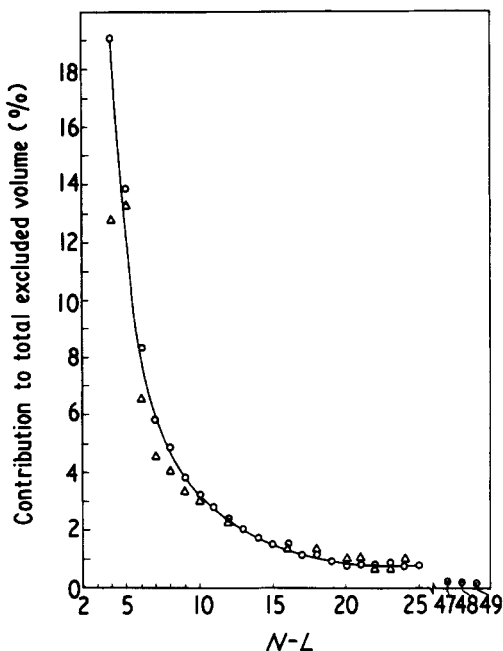
Samples of fifty 500-link chains were generated, one with freely varying and the other with fixed bond angles, at  $v = 0.2, 0.3, 0.4, \dots, 1.0$  in the former case and  $v = 0.2, 0.4, \dots, 1.0$  in the latter. It was found for each chain that, once it had exceeded a length of approximately 50 links, the contribution to the total excluded volume from recently generated monomers, say up to 25 links away, whilst varying with recency of generation, did not alter as the chain length increased. Averages were therefore taken over all chains in the sample, beyond the 100th link, yielding the average percentage excluded volume due to monomers 1, 2, 3,  $\dots$ , 49, or more links away. (Exclusions due to individual monomers fifty or more links away occurred so infrequently that averages were meaningless; hence their lumping together.) The variation of percentage exclusion due to individual monomers, as a function of their recency of generation  $N - L$ , is shown in figures 12 and 13 for the two different geometries.

Considering first the chains with freely varying bond angles, the curves of figure 12 are readily divisible into two parts, namely a steep descent at low  $N - L$  values followed by a much slower fall-off at higher  $N - L$ . It will be seen that the percentage contribution to the total exclusion at higher  $N - L$  increases as  $v$  decreases. However, even at  $v = 0.2$ , only 0.75% of the total exclusion is due to monomers fifty or more links away. It should also be noted that, if a particular monomer contributes to the partial exclusion of a site fifty or more links away, its contribution is independent of  $v$ , fluctuating about a mean of 0.6%. In order to attempt to determine the asymptotic behaviour of the percentage contributions at large  $N - L$ , chains of 1000 links were built. If the average contribution from each atom has reached, or is still approaching, some nonzero asymptotic value, then the percentage exclusion due to monomers fifty or more links away should be greater in 1000-link chains than in the 500-link chains to which figure 12 refers. However, when the chains were analysed in segments of 200 links it was found that, apart from random fluctuations, no consistent trends or differences were discernible, even though there are 750 to 950 monomers 50 or more links away in the last segments ( $N = 800-1000$ ) compared with only 50 to 150 in the first segment ( $N = 1-200$ ). This result must not, however, be interpreted to mean that the contribution to the total excluded volume is zero from monomers more than 200 links away, since exclusions were found due to monomers distant as much as 843 links. A possible interpretation is that contributions to the total excluded volume from very distant monomers occur at random, ie independent of  $N - L$  but that the total contribution is constant. Certainly any increase in total excluded volume with increasing chain length must be very slow.

As  $v$  increases from 0.2 to 0.6 in chains with fixed bond angles, a slight increase in the contributions from monomers four and five links distant occurs, and this tendency



**Figure 12.** Variation in percentage contribution to total excluded volume from monomers  $L$  with their recency of generation  $N-L$ , for freely varying bond angle chains at various values of  $v$ . Inset shows 0–100%.



**Figure 13.** Variation in percentage contribution to total excluded volume from monomers  $L$  with their recency of generation  $N-L$ , for fixed bond angle chains, at  $v = 0.6$  ( $\Delta$ ) and  $1.0$  ( $\circ$ ).

is seen in figure 13 to persist up to  $v = 1.0$ . The behaviour of chains with fixed bond angles is similar to that of freely varying bond angle chains in two aspects, namely: (i) the percentage contributions to the excluded volume decrease rapidly with increasing  $N-L$  at low  $N-L$ ; (ii) the percentage contribution to exclusion from individual monomers ten or more links away is independent of  $v$ , fluctuating about a mean of 0.9% (cf 0.6% from individual monomers fifty or more links away, in the freely varying case). The two types of chains differ in that, while the percentage contribution in the freely varying case decreases with increasing  $v$  over the  $N-L$  range 5–50, the curves for varying  $v$  coincide in the fixed case for  $N-L$  in the range 10–50.

It will now be clear that there are two main contributions to the total excluded volume, namely a dominant ‘short-range’ effect dependent on both chain-model and  $v$ , and a ‘long-range’ effect dependent only very slightly (if at all) on chain-model and  $v$ . It seems an obvious step to associate the short-range effect with the so called intrinsic excluded volume (IEV) suggested by Windwer (1965), and the long-range effect with his extrinsic excluded volume (EEV). The IEV is the hard core excluded by the monomer units themselves, ie in the present calculations it is related to the volume of the individual spheres representing the monomers. The EEV comes into play when the chain coils in such a way as to exclude a volume which is much greater than the sum of the volumes of the individual monomers constituting the coil. However, while a correlation between IEV and excluded volume ratio  $v$  is readily justified, it is not immediately obvious why EEV should be nearly independent of  $v$ .

#### 4. End-to-end length distribution function

A complete specification of the configurational properties of polymer chains includes the distribution of these properties about their mean values as well as the mean values themselves. Consequently the distribution of the end-to-end distance  $R$  was investigated.

Averages of four higher-order moments of  $R$ , namely  $\langle R_N^3 \rangle$ ,  $\langle R_N^4 \rangle$ ,  $\langle R_N^6 \rangle$ , and  $\langle R_N^8 \rangle$ , and also  $\langle R_N \rangle$ , were obtained from two sets of one thousand 100-link chains, with freely varying and fixed bond angles respectively, using the inversely restricted sampling technique.

Defining reduced moments  $\delta_N(p, s)$  by

$$\delta_N(p, s) = \frac{\langle R_N^p \rangle}{\langle R_N^s \rangle^{p/s}},$$

values of  $\delta_N(2, 1)$ ,  $\delta_N(4, 2)$ ,  $\delta_N(6, 2)$ ,  $\delta_N(6, 3)$ ,  $\delta_N(8, 2)$  and  $\delta_N(8, 4)$  were calculated. Limiting values  $\delta_\infty(p, s)$  were obtained by fitting the  $\delta_N(p, s)$  to the equation

$$\delta_N(p, s) = a(p, s) + \frac{b(p, s)}{N} \quad (6)$$

and then equating  $\delta_\infty(p, s)$  to  $a(p, s)$ . The low-order equation (6) was chosen following Mazur and McCrackin (1968), who reported that this equation yielded 'better' extrapolations than others involving higher-order polynomials in  $(1/N)$ . We present in figure 14 the variation of  $\delta_N(2, 1)$  with  $N$  for  $v = 0.4$ , in order to show how the reduced moments oscillate within relatively small limits of their asymptotic values around  $N = 100$ . The differences  $\delta_N - \delta_{N-1}$  decrease rapidly with increasing  $N$ , being of order  $10^{-3}$  for  $\delta_N(2, 1)$ ,  $\delta_N(4, 2)$  and  $\delta_N(6, 3)$  at  $N = 100$ , and of order  $10^{-2}$  for the higher-order moments which are subject to greater error.

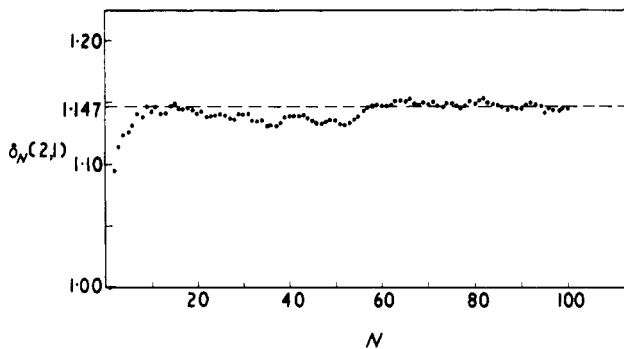


Figure 14. Variation of  $\delta_N(2, 1)$  with  $N$  for freely varying bond angle chains at  $v = 0.4$ .

Table 4 shows the limiting  $\delta_\infty(p, s)$  values obtained for a range of  $v$ -values, along with the corresponding values for the Gaussian distribution function  $W(R)$  of the end-to-end distance  $R$ , namely

$$\lim_{N \rightarrow \infty} W(R) = 4\pi R^2 \left( \frac{3}{2\pi N b^2} \right)^{3/2} \exp\left( \frac{-3R^2}{2N b^2} \right), \quad (7)$$

each step being of length  $b$ . The latter represents the zero excluded volume case. It will be seen that, in general, the  $\delta_\infty$  values decrease steadily with increasing  $v$ .



**Table 4.** Variation of reduced moments  $\delta_{\infty}(p, s)$  with  $v$ .

$v$	$\delta_{\infty}(2, 1)$	$\delta_{\infty}(4, 2)$	$\delta_{\infty}(6, 3)$	$\delta_{\infty}(6, 2)$	$\delta_{\infty}(8, 4)$	$\delta_{\infty}(8, 2)$
Freely varying bond angles						
0.2	1.172	1.636	2.471	3.660	3.866	10.232
0.3	1.153	1.561	2.291	3.263	3.527	8.481
0.4	1.147	1.523	2.151	3.012	3.126	7.160
0.5	1.136	1.477	2.024	2.772	2.836	6.155
0.6	1.128	1.448	1.972	2.652	2.789	5.797
0.7	1.128	1.446	1.953	2.628	2.705	5.622
0.8	1.124	1.429	1.909	2.544	2.597	5.264
0.9	1.125	1.434	1.913	2.561	2.591	5.311
1.0	1.123	1.417	1.867	2.474	2.503	4.991
Fixed bond angles						
0.2	1.162	1.576	2.270	3.275	3.342	8.241
0.4	1.146	1.525	2.159	3.026	3.138	7.227
0.6	1.132	1.463	1.997	2.709	2.779	5.903
0.8	1.119	1.411	1.860	2.455	2.489	4.925
1.0	1.110	1.378	1.792	2.318	2.390	4.505
Gaussian distribution (zero excluded volume)						
0.0	1.178	1.667	2.577	3.889	4.200	11.667

We now propose a radial distribution function of the general form (Mazur 1965a, b)

$$W(R) = BR^l \exp\left[-\left(\frac{R}{\sigma}\right)^t\right] \tag{8}$$

where  $B$ ,  $l$ , and  $t$  are constants, and  $\sigma$  is a scaling factor.

Hence

$$\delta_{\infty}(p, s) = \frac{\langle R^p \rangle}{\langle R^s \rangle^{p/s}} = \frac{\Gamma((l+p+1)/t) [\Gamma((l+1)/t)]^{(p/s)-1}}{[\Gamma((l+s+1)/t)]^{p/s}} \tag{9}$$

where  $\Gamma(x)$  is the gamma function defined by

$$\Gamma(x) = \int_0^{\infty} h^{x-1} \exp(-h) dh \quad (x > 0).$$

The most suitable pairs of parameters  $l$  and  $t$  in the distribution function (equation (8)) were found by comparing the six 'experimental' moment values  $\delta_{\infty}(p, s)$  of table 4 with those predicted from equation (9). A computer program was written in which  $t$  was varied over the range 2.0–4.0 ( $t = 2.0$  for a Gaussian distribution); for each value of  $t$ , and for each moment,  $l$  was chosen so as to minimize  $|\delta_{\infty\text{calc}} - \delta_{\infty\text{exp}}|$ . The values were then plotted against  $t$  for each of the six moments, and the 'intersection' of the six curves was chosen as the best  $(l, t)$  combination. The resulting data for all values of  $v$  are given in table 5.

Table 5. Parameters  $l$  and  $t$  of the distribution function  $W(R)$ .

$v$	Freely varying bond angles		Fixed bond angles	
	$l$	$t$	$l$	$t$
0.2	1.90	2.16	1.77	2.57
0.3	2.14	2.27		
0.4	1.88	2.74	2.00	2.60
0.5	1.95	2.96		
0.6	2.11	3.00	1.98	3.03
0.7	2.04	3.12		
0.8	1.98	3.33	2.04	3.46
0.9	1.93	3.38		
1.0	1.94	3.52	2.18	3.62
	Mean = 1.99		Mean = 1.99	

It will be seen that  $l$  fluctuates, in an apparently random fashion, around a mean value of approximately 2.0, but  $t$  increases steadily with increasing  $v$ , for both geometries.  $t$  is, of course, 2.0 for zero excluded volume. We therefore suggest that a distribution function of the form proposed by Mazur (1965a, b), namely

$$W(R) = BR^2 \exp\left[-\left(\frac{R}{\sigma}\right)^t\right],$$

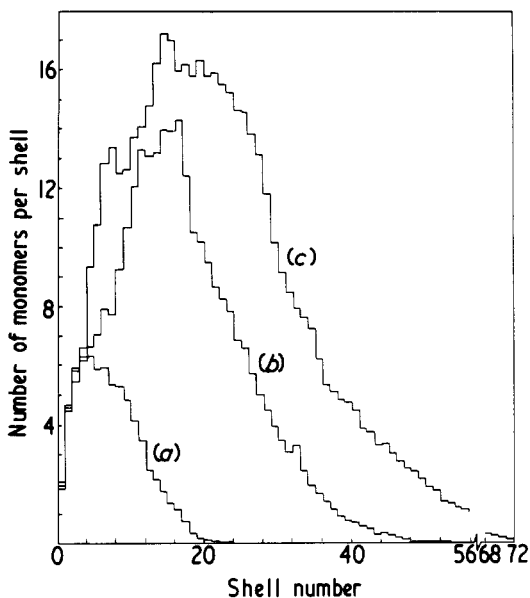
is more appropriate than that of Domb *et al* (1965) given by

$$W(R) = CR^t \exp\left[-\left(\frac{R}{\sigma}\right)^t\right]$$

since there is no indication that  $l = t$ . It should also be noted here that the relationship  $t = 2/(2-\gamma)$  proposed by Fisher (1966) does not hold, the discrepancy increasing with  $v$ .

The distribution function indicates the range of end-to-end lengths which can occur among the many possible chain configurations for specified values of  $v$  and  $N$ . It is also of interest to know how the individual monomers are spatially distributed within a given chain. In this context the storage table described by Fleming (1967) in connection with checking for violation of the excluded volume conditions is of value. This table shows the number of monomers situated in shells between 0 and 1, 1 and 2, 2 and 3, etc units of length from the origin, and their precise locations within those shells. Hence if a cumulative total of the number of monomers in each annulus is obtained for a large number of chains, a reliable indication of the average spatial distribution of the monomers within the chains can be derived. Unfortunately the method of inversely restricted sampling does not lend itself to such a procedure, since the different statistical weights occurring along the chains render the averaging procedure too complex. However, the results obtained using the sample enrichment technique can be treated in the manner described, and figure 15 shows three histograms of the number of monomers in a given shell against the position of that shell, for freely varying bond angles at  $v = 0.5$ . The corresponding  $\langle R \rangle$  values are also indicated. These histograms show the density of monomers as a function of distance from the origin, independent

of direction. The distribution would be expected to be spherically symmetric (Domb *et al* 1965), and a rough check that  $\Sigma x$ ,  $\Sigma y$ , and  $\Sigma z$  were each zero, when summed over all 504 links in a two thousand nine hundred chain sample, confirmed this expectation.



**Figure 15.** Average distribution of monomers within (a) 72-link ( $\langle R \rangle = 11.47$ ), (b) 288-link ( $\langle R \rangle = 22.94$ ) and (c) 504-link ( $\langle R \rangle = 30.35$ ), freely varying bond angle chains at  $v = 0.5$ , sample containing two thousand nine hundred chains.

### 5. Discussion

The results presented in this paper support the conclusion of Windwer (1965), Gallacher and Windwer (1966), and Mark and Windwer (1967) that real finite polymer-chain systems must be considered individually in order to obtain the dependence of their configurational properties on the number of monomers in the chain. This conclusion is opposed to the widely held view, eg Domb (1963, 1969), Edwards (1965) that the effects of excluded volume on the dimensions of finite polymer chains are completely specified by the dimensionality of the chains. Thus, according to Domb,  $\langle R_N^2 \rangle \propto N^{6/5}$  in three dimensions, and  $\langle R_N^2 \rangle \propto N^{3/2}$  in two dimensions. Furthermore, it is claimed (Domb 1969, 1970, Martin 1970) that asymptotic behaviour is attained, for three-dimensional on-lattice chains, for  $N$  as low as 15; although some of the corresponding results in two dimensions (eg Wall and Erpenbeck 1959) are erratic, since sample attrition is more serious in two dimensions, little deviation from the  $N^{3/2}$  law is expected for  $N > 500$ . Edwards (1965), using a self-consistent field technique similar to that introduced by Hartree for atomic wavefunctions, also obtained the  $N^{6/5}$  law in three dimensions, and claimed that such behaviour would be obtained if  $N \gg L^6/V^2$ , where  $L$  is the bond length and  $V$  the excluded volume. On a lattice model  $L$  corresponds roughly to the lattice spacing and  $V$  to the unit cell volume. Thus asymptotic behaviour would be expected around  $N = 10$  for most three-dimensional lattices. On the continuum model, if we take  $L$  as the separation between the centres of consecutive spheres,

and  $V$  as four times the volume of each sphere, then asymptotic behaviour would be expected if  $N \gg 3750$  at  $v = 0.2$ ,  $N \gg 16$  at  $v = 0.5$ , and  $N \gg 1$  at  $v = 1.0$ .

The present results suggest that, for continuum model chains up to  $N = 500$ , the exponents  $\gamma$  and  $\gamma'$  are not determined uniquely by dimensionality. Rather they tend to increase monotonically with  $v$ , as also does the parameter  $t$  in the end-to-end distribution function  $W(R)$  of equation (8). One must consider the possibility that, as  $N \rightarrow \infty$ ,  $\gamma$  and  $\gamma'$  will attain a value independent of  $N$ , and that  $t$  will also become independent of  $v$ . Monte Carlo calculations cannot, of course, be extended to the limit  $N \rightarrow \infty$ , and therefore such asymptotic behaviour must still be regarded as a theoretical possibility. However, chains of infinite length have no practical interest; the present work strongly suggests that, for chains of intermediate length, say up to  $N = 500$ , which are of practical interest,  $\gamma'$  and  $t$  are each dependent on  $v$ . If  $\gamma$ ,  $\gamma'$  and  $t$  become independent of  $v$  in longer chains, then the approach to such behaviour must be very slow. It should also be stated that a monotonic increase in these three parameters with increasing  $v$  seems intuitively more acceptable than a discontinuity, eg in  $\gamma$  and  $\gamma'$  between unity and  $\frac{6}{5}$ , when excluded volume, no matter how small, is taken into account.

The discrepancy between the results for on-lattice and continuum-model chains can perhaps be explained in two ways. Either a rigorous analytical treatment of the problem would show that all chains of the same dimensionality, whether on- or off-lattice, have the same asymptotic configurational behaviour, and the continuum-model chains of the present work approach that limit very slowly, or one or more of the approximations in the analytical treatments published to date implies a fundamental similarity to lattice-constrained behaviour. As stated immediately above, the first explanation cannot be completely discounted, but, in view of the apparent attainment of asymptotic behaviour not later than  $N = 200$ , it seems unlikely. With reference to the second explanation it may be that approximate analytical treatments (eg Edwards 1965, Reiss 1967), which regard a polymer chain as consisting of a number of segment clouds, are inadequate because the envisaged repulsive interaction between neighbouring segment clouds does not take into account the covalent binding between consecutive monomers of the chain, ie orientation restrictions arising from fixed bond angles and bond lengths are ignored. Furthermore, the possibility of chain coiling so as to exclude a volume much larger than the sum of the volumes of the individual monomers of the coil, ie the EEV effect of Windwer (1965), appears to be ignored. Thus the only long-range effect of excluded volume operative is that associated with IEV, ie the hard cores of the individual monomers. It is easy to see how the long-range effect of IEV could be independent of  $v$ ; a difference of, say, 0.25 units in the radius of a monomer situated near the end of a given chain is unlikely to be significant in relation to the probability of volume interference of that monomer with another near the chain origin. Supporting evidence was presented in § 3, where the amount of volume interference between monomers separated by a large number of intermediate links was shown to be independent of  $v$ . Thus it seems reasonable to suppose that, if EEV effects are absent, the total long-range excluded volume effect will be independent of  $v$ .

While it may be true that the analytical calculations do not allow for EEV effects due to bonding, these effects would certainly be expected to occur in lattice-constrained chains. As far as IEV effects are concerned, it is helpful to consider the chain generation process as a Markov process of order  $r$ . We can identify two cases:

(i)  $r \gg N$ . Each monomer added to the chain is then influenced by the presence of each previously added monomer, and we would certainly expect the resulting increase in  $\gamma$  to be lattice-dependent.

(ii)  $r \ll N$ . Each monomer interacts only with those monomers distant not more than  $r$  links along the chain, and consequently the configurational properties of the chain do not differ significantly from those of a completely random walk (Domb 1969). In particular,  $\langle R_N^2 \rangle$  acquires an expansion factor independent of  $N$ , and end-correction terms of order less than  $N$ , so that  $\langle R_N^2 \rangle \sim C_r N$ . What might be considered as the long-range effects of IEV are therefore absent, and any increase in  $\gamma$  must be due to EEV effects. These were found to be almost independent of  $v$  in continuum-model chains. Hence if it is correct to identify excluded volume with unit cell volume, we might expect a lattice-independent increase in  $\gamma$  for the lattice model chains.

The values of  $r$  for chain generation on lattices are generally agreed to be small. Thus if the corresponding values for real polymer chains are much larger, lattice models of such chains could be unsatisfactory.

## 6. Conclusions

The following conclusions may be drawn from the results presented in this paper:

(i) For chains of less than 100 links, the exponents  $\gamma$  and  $\gamma'$  in the equations  $\langle R_N^2 \rangle = aN^\gamma$  and  $\langle S_N^2 \rangle = a'N^{\gamma'}$  tend to increase monotonically from unity as the sphere diameter  $v$  increases from zero to unity. The coefficients also vary with  $v$  and the chain geometry.

(ii) The expansion factor  $\alpha^2(z)$  does not consistently follow any of the published two-parameter curves.

(iii) The ratio  $\langle S_{100}^2 \rangle / \langle R_{100}^2 \rangle$  decreases slowly from 0.167 at zero excluded volume to about 0.157 for  $N \geq 0.6$ , these values being very close to those published for on-lattice chains.

(iv) The distribution function  $W(R)$  of the probability that the end-to-end length of a chain will be  $R$  can be expressed as  $W(R) dR = KR^2 \exp[-(R/\sigma)^t] dR$  where  $K$  and  $\sigma$  are constants, the latter being directly proportional to the mean square end-to-end length of the chain, and  $t$  is a parameter which increases monotonically with increasing excluded volume from a value of 2.0 at zero excluded volume.

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